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(54) Fluorocarbon elastomer composition

(57) A fluorocarbon elastomer composition comprising a fluorocarbon-elastomer gum, and fluorinated ether composition comprising a functional fluoroaliphatic mono-or polyether of linear and regular structure, wherein said functionality is reactive with said gum and is selected from the group consisting of primary amino, and allyl- $(-CH_2-CH=CH_2)$. The fluorocarbon elastomer composition is compounded, then shaped and heated to form a cured, shaped article such as automotive fuel line hose or O-ring.

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Description

This invention relates to fluorocarbon elastomers and their curing. In another aspect it relates to fluorinated ether compositions used in curing fluorocarbon elastomers. In another aspect it relates to fluorocarbon gum composition containing fluorinated ether compositions. In a further aspect it relates to a cured, shaped article of fluorocarbon elastomer, such as automotive fuel line hose and O-ring seals.

Fluorocarbon elastomers are synthetic elastomeric polymers with a high fluorine content - see, for example, West, A.C. and Holcomb, A.G., "Fluorinated Elastomers," Kirk-Othmer, Encyclopedia of Chemical Technology, Vol. 8, pp. 500-15 (#3rd ed., John Wiley & Sons, 1979). Fluorocarbon elastomers, particularly the copolymers of vinylidene fluoride with other ethylenically unsaturated halogenated monomers, such as C_3F_6 (hexafluoropropene) have become the polymers of choice for high temperature applications, such as seals, gaskets, and linings, especially when shaped articles thereof are subject to exposure to aggressive or harsh environments, such as solvents, lubricants, and oxidizing or reducing conditions. A major drawback to many applications of shaped articles made of such fluorocarbon elastomers has been their inability to satisfactorily function at low temperatures. At temperatures only slightly below $0^\circ C$, the articles become stiff and fail to perform satisfactorily. Many fluoroelastomers also exhibit a tendency to become "scorchy", i.e., they cure prematurely or too rapidly when compounded. Fluoroelastomers may also adhere to dies upon curing making removal of the shaped fluoroelastomer article difficult.

Such fluorocarbon elastomers in general can be compounded and cured to have high tensile strength, good tear resistance, and low compression set. Such compounded polymers are typically fabricated into automotive engine oil seals, fuel system components, such as fuel line hoses and O-ring seals, and drive train seals. Smaller, hotter-running automotive engines, modern fuel blends, and aggressive oil additives and other chemical substances used in operating the engines have made fluorocarbon elastomers the polymers of choice for a host of elastomeric engine components where reliable sealing is required and of environmental concern - see Brullo, R.A., "Fluoroelastomer Rubber for Automotive Applications", Automotive Elastomer & Design, June 1985, and "Fluoroelastomers Seal Up Automotive Future," Materials Engineering, October, 1988.

Most commercially available fluorocarbon elastomers, such as the illustrative polymers described above are sold, for example, under the trademarks "AFLAS", "FLUOREL" and "VITON". Some of these are crosslinked with aromatic polyhydroxy compounds, such as bisphenols, which are compounded with the elastomer gum along with a curing accelerator, such as a quaternary phosphonium salt, and acid acceptors, such as magnesium oxide and calcium hydroxide - see, for example, U.S. Pat. No. 4,287,320 (Kolb). Others are bromine-containing, peroxide-curable fluorocarbon elastomers - see U.S. Pat. Nos. 4,035,565 (Apotheker et al.) and 4,450,263 (West).

Several general types of fluorinated ethers have been described in the literature. One type is characterized by one of several homopolymeric segments or blocks of repeating units of the formula $-CF(CF_3)CF_2O-$ and made from hexafluoropropylene epoxide, see e.g., U.S. Pat. No. 3,250,807 (Fritz et al.). Another type is that characterized by blocks of repeating units of the formula $-CF_2CF_2O-$ and made from tetrafluoroethylene epoxide, see for example, U.S. Pat. No. 3,125,599 (Warnell). Others, made by reacting oxygen with tetrafluoroethylene or hexafluoropropylene, are characterized by a backbone made of repeating $-CF_2O-$ units, see e.g., U.S. Pat. No. 3,392,097 (Carraro et al.), or $-CF(CF_3)CF_2O-$ units, see e.g., U.S. Pat. No. 3,442,942 (Sianesi et al.), or, in addition to either of these units, units of the formula $-CF(CF_3)O-$, see e.g., U.S. Pat. No. 3,699,145 (Sianesi et al.), or a backbone consisting of randomly distributed $-CF_2O-$ and $-CF_2CF_2O-$ units, see e.g. U.S. Pat. No. 3,715,378 (Sianesi et al.), or a backbone made up of $-CF(CF_3)CF_2O-$ and $-CF_2CF_2O-$ units and, optionally, $-CF_2O-$ and $-CF(CF_3)O-$ units. Another type of fluorinated ether is that characterized by backbone units of the formula $-(CF_2)_aO(CF_2)_b-$ made by photopolymerization, see e.g., U.S. Pat. No. 3,504,411 (Rice) and U.S. Pat. No. 3,849,594 (Mitsch et al.).

U.S. Pat. Nos. 3,810,874 (Mitsch et al.) and 4,094,911 (Mitsch et al.) disclose poly(perfluoroalkylene oxides) terminated with polymerizable functional groups which can be polymerized to prepare certain polymers, e.g. polyurethanes, having low glass transition temperatures and low-temperature flexibility. U.S. Pat. No. 3,810,875 (Rice et al.) discloses use of poly(perfluoroalkylene oxide) peroxides with ethylenically unsaturated monomers in making block copolymers having good low-temperature flexibility. Fluorinated ethers with nonfunctional terminal moieties are sold under the trademarks "KRYTOX" and "FOMBLIN" for use as vacuum pump fluids, see e.g., G. Caporiccio et al., Ind. Eng. Chem. Prod. Res. Dev. 1982, 21, 515-19.

U.S. Pat. No. 4,810,760 (Strepparola et al.) discloses compositions of fluoroelastomers crosslinked with dihydroxypolyfluoroethers. The dihydroxypolyfluoroethers of Strepparola contain either branched moieties, or are random copolymers containing $-CF_2O-$ repeating units, or contain partially fluorinated repeat units. When used to crosslink fluorocarbon elastomers, the fluorinated ethers of Strepparola are said to give materials with improved heat stability and greater resistance to compression set. U.S. Pat. No. 4,894,418 (Strepparola et al.) discloses compositions of fluoroelastomers comprising, as a processing coadjuvant, a mono- or dihydroxypolyfluoroether. These mono- or dihydroxypolyfluoroethers have similar structures to those disclosed in U.S. Pat. No. 4,810,760 (Strepparola et al.). The addition of these mono- or dihydroxypolyfluoroethers to conventional vulcanizable fluoroelastomer compositions is said to

improve the processability of the resulting mixture and the low temperature brittle point of the cured mixture.

U.S. Pat. No. 3,632,788 (Stivers et al.) discloses fluoro-olefinic elastomeric formulations with improved low temperature flexibility and softness. The improved properties are imparted by the incorporation of one or more low melting low molecular weight, polar, fluoroaliphatic compounds.

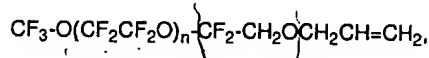
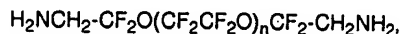
5 U.S. Pat. No. 5,026,786 (Marchionni et al.) discloses a process for the manufacture of certain perfluoropolyethers. These perfluoropolyethers comprise randomly distributed perfluoroalkylene units. These perfluoropolyethers are said to improve the extrudability of elastomer compositions and to decrease the adhesion of vulcanized articles to molds.

U.S. Pat. No. 4,278,776 (Mauro et al.) discloses vulcanizable mixes based on fluoroelastomer and which comprise, as a processing aid, at least one fluorinated polyamide. Certain perfluoropolyethers are said to improve the low temperature properties of the vulcanisates.

10 European Pat. Pub. No. 222,201 (Tommasi et al.) discloses vulcanizable rubber blends comprising certain perfluoropolyethers. These perfluoropolyethers have brominated or fluorinated end groups. These blends are said to have improved processability.

European Pat. Pub. No. 310,966 (Arcella et al.) discloses rubber blends comprising certain perfluoropolyethers. 15 These perfluoropolyethers comprise perfluoroalkyl end groups. These rubber blends are said to have improved mold-release properties.

Briefly, in one aspect, this invention provides a fluorocarbon elastomer composition comprising (1) fluorocarbon elastomer gum, such as a copolymer of vinylidene fluoride and hexafluoropropene, and (2) a fluorinated ether composition comprising a functional fluoroaliphatic mono- or polyether, of linear and regular structure, wherein said functionality is reactive with said gum and is selected from the group consisting of primary amino, and allyl (-CH₂-CH=CH₂), e.g.



25 In a further aspect of this invention there is provided a method of preparing an elastomer composition, said method comprising mixing the afore-mentioned (1) fluorocarbon elastomer gum and (2) a fluorinated ether composition as defined above.

The functional fluoroaliphatic mono- or polyether comprises a perfluoroether structure which consists or consists 30 essentially of two or more perfluoroalkylene moieties, e.g. -CF₂- and -CF₂CF₂-, bonded together by ether oxygen atoms in a linear (or non-branched), regular (or non-random), divalent, and acyclic perfluoroether structure, e.g. a perfluoroalkyleneoxyalkylene. Each end of the perfluoroether structure is bonded to a terminal group, at least one of such terminal groups having a functional moiety reactive with said fluorocarbon elastomer gum. Examples of terminal groups include

35 -CH₂NH₂, and -C(O)NHCH₂CH=CH₂. Said fluorinated ether composition acts as a low-temperature flexibilizer and imparts improved low-temperature flexibility to the cured fluorocarbon elastomer composition.

The fluorinated ether composition imparts improved mold-release properties to the cured fluorocarbon elastomer composition.

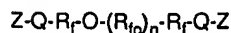
The fluorocarbon elastomer composition can be compounded to be resistant to scorch during curing.

40 A first class of fluorinated ether compositions is that where there is an average number of said reactive terminal groups per fluorinated ether molecule of greater than 1.0 and less than or equal to 2.0. A second class of fluorinated ether compositions is that where there is an average number of said reactive terminal groups per fluorinated ether molecule of less than or equal to 1.0.

The above fluorocarbon elastomer gum and fluorinated ether composition can be compounded or mixed in one or 45 several steps, and then the mixture can be processed and shaped, for example, by extrusion (for example, in the form of a hose or hose lining) or molding (for example, in the form of an O-ring seal). The shaped article can then be heated to cure the gum composition and form a cured elastomer article. When the fluorinated ether composition used in a reactive mixture with the fluorocarbon elastomer gum is of said second class, the resulting composition is further compounded with a crosslinking agent, for example, 2,2-bis-(4-hydroxyphenyl) hexafluoropropane, to obtain a curable composition

50 The cured fluorocarbon elastomer mixture, containing either class of fluorinated ether composition, has excellent low-temperature flexibility while retaining the desired physical properties, for example tensile strength and elongation, of conventionally compounded and cured fluorocarbon elastomer compositions. Particularly useful articles that can be fabricated from the fluorocarbon elastomer compositions of this invention are fluorocarbon elastomer automotive components, such as those described in the two above cited journal articles of Brullo, e.g., fuel line hoses.

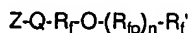
Said first class of fluorinated ether composition useful in this invention comprises functional fluorinated ethers which can be represented by the Formula



In formula I, $-R_f-O-(R_{fo})_n-R_f-$ represents one type of said perfluoroether structure and Z-Q- represents the terminal groups, where Q is a divalent linking group and Z is a moiety reactive with said fluorocarbon elastomer. The average number of Z groups per fluorinated ether molecule of this class is greater than 1.0 and less than or equal to 2.0. Said Z group is selected from the group of members consisting of

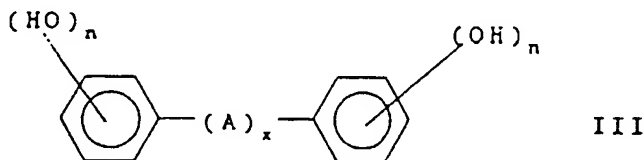
primary amino, and allyl ($-\text{CH}_2-\text{CH}=\text{CH}_2$). The divalent linking group Q is preferably selected from the group consisting of $-\text{CO}-$, $-\text{O}-$, $-\text{SO}_2-$, $-\text{C}_y\text{H}_{2y}-$ where y is 1 to 20, $-\text{C}_6\text{H}_4-$, $-\text{C}_6\text{H}_3\text{Cl}-$, $-\text{OC}_2\text{H}_4-$, $-\text{CONR}-$ or $-\text{SO}_2\text{NR}-$ where R is lower alkyl of 1 to 3 carbon atoms, or combinations of said groups such as $-\text{CH}_2\text{CO}-$. However, when Q is said $-\text{CO}-$, $-\text{O}-$, $-\text{CONR}-$, $-\text{SO}_2\text{NR}-$, or $-\text{SO}_2-$, then Z is allyl. R_f is a non-branched, perfluoroalkylene group of 1 to 20 carbon atoms. R_{fo} is a perfluoroalkyleneoxy group selected from the group consisting of $-(\text{CF}_2)_2\text{O}-$, $-(\text{CF}_2)_3\text{O}-$, $-(\text{CF}_2)_4\text{O}-$, $-\text{CF}_2\text{CF}_2\text{O}-$, $-\text{CF}_2\text{CF}_2\text{O}-\text{CF}_2\text{CF}_2\text{O}-\text{CF}_2\text{CF}_2\text{O}-$. The subscript n is a number from 0 to 30. When n is greater than 1.0, $(R_{fo})_n$ is a homopolymer.

Said second class of fluorinated ether composition useful in this invention comprises functional fluorinated ethers which can be represented by the Formula



In formula II, $-R_f-O-(R_{fo})_n-$ represents one type of said perfluoroether structure, Z, R_f , R_{fo} , n, and Q are as described above for formula I. The average number of Z groups per fluorinated ether molecule of this class is less than or equal to 1.0. R_f' is a nonbranched, monovalent, fluoroaliphatic group containing from 1 to 10 carbon atoms. The fluorocarbon elastomer compositions of the present invention may be further compounded, and cured according to standard methods. In order to form cured articles, the compositions of the present invention comprising the fluorochemical ether compositions of the second class, represented by Formula II, will need to be further compounded with a crosslinking agent, either the fluorinated ether composition, represented by Formula I, of this invention or with a conventional cure system, such as a polyhydroxy, or a peroxide cure system.

The most common crosslinking agent for fluorocarbon elastomer gum is a polyhydroxy compound. The polyhydroxy compound used in its free or non-salt form and as the anionic part of the salt component of the crosslinking agent can be any of those polyhydroxy compounds known in the art to function as a crosslinking agent or co-curable for fluoroelastomers, such as those polyhydroxy compounds disclosed in U.S. Pat. Nos. 4,259,463 (Moggi et al.), 3,876,654 (Pattison), 4,233,421 (Worm), and U.S. Defensive Publication T107,801 (Nersasian). For example, representative aromatic polyhydroxy compounds include any one of the following: di-, tri-, and tetrahydroxybenzenes, naphthalenes, and anthracenes, and bisphenols of the Formula

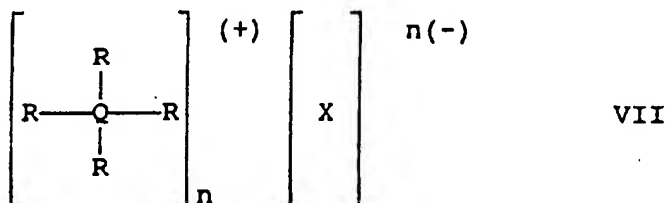


wherein A is a difunctional aliphatic, cycloaliphatic, or aromatic radical of 1 to 13 carbon atoms, or a thio, oxy, carbonyl, sulfonyl, or sulfonyl radical, A is optionally substituted with at least one chlorine or fluorine atom, x is 0 or 1, n is 1 or 2, and any aromatic ring of the polyhydroxy compound is optionally substituted with at least one atom of chlorine, fluorine, or bromine atom, or carboxyl or an acyl radical (e.g., $-\text{COR}$, where R is H or a C_1 to C_8 alkyl, aryl or cycloalkyl group) or alkyl radical with, for example, 1 to 8 carbon atoms. It will be understood from the above bisphenol Formula III that the $-\text{OH}$ groups can be attached in any position (other than number one) in either ring. Blends of two or more such compounds can also be used. One of the most useful aromatic polyphenols is the bisphenol compound known as Bisphenol AF, which is 2,2-bis(4-hydroxyphenyl)hexafluoropropane. The compounds 4,4'-dihydroxydiphenyl sulfone (Bisphenol S) and 2,2-bis(4-hydroxyphenyl)propane (Bisphenol A) are also considered useful in this invention. Another useful aromatic polyhydroxy compound is hydroquinone. Others are dihydroxybenzenes such as catechol, resorcinol, 2-methyl resorcinol, 5-methyl resorcinol, 2-methyl hydroquinone, 2,5-dimethyl hydroquinone, and 2-t-butyl hydroquinone, 1,5-dihydroxynaphthalene and 9,10-dihydroxyanthracene.

Representative aliphatic polyhydroxy compounds include fluoroaliphatic diols, e.g. 1,1,6,6-tetrahydrooctafluorohexanediol, and others such as those described in U.S. Pat. No. 4,358,559 (Holcomb et al.) and references cited therein. Derivatives of polyhydroxy compounds can also be used such as those described in U.S. Pat. No. 4,446,270 (Guenth-

ner et al.) and include, for example, 2-(4-allyloxyphenyl)-2-(4-hydroxyphenyl)propane. Mixtures of two or more of the polyhydroxy compounds can be used.

The organo-onium compound which can be incorporated into or compounded with the fluoroelastomer gum as a co-curing agent or vulcanization accelerator include those known and described in the art - see, for example, the description of such organo-onium compounds in U.S. Pat. No. 4,882,390 (Grootaert et al.) The organo-onium compounds which can be used include quaternary organo-onium compounds, such as ammonium, arsonium, phosphonium, stibonium, amino-phosphonium, phosphorane (e.g., triarylphosphorane), and iminium compounds, and sulfonium compounds. Mixtures of organo-onium compounds are also useful in this invention. The ammonium, phosphonium, arsonium, and stibonium salts or compounds preferably have the general formula:



where Q is nitrogen, phosphorous, arsenic or antimony; X is an organic or inorganic anion (e.g., halide, sulfate, acetate, phosphate, phosphonate, hydroxide, alkoxide, phenoxide, or bisphenoxide); n is equal to the valence of the anion X; and each R is independently an alkyl, aryl, alkenyl, or combinations thereof. Each R can be substituted with chlorine, fluorine, bromine, cyano, -OR' or -COOR' where R' is a C₁ to C₂₀ alkyl, aryl, aralkyl, or alkenyl. Any pair of the R groups can be connected with each other and with the Q atom to form a heterocyclic ring. A preferred organo-onium compound where the aromatic polyhydroxy compound used is Bisphenol AF, is where in formula VII the Q is phosphorous, X is a chloride anion, n is 1, and three of the R groups are phenyl moieties and the remaining R group is a benzyl moiety. A preferred class of formula VII is where at least one of the R groups is alkyl or alkenyl. In another class of quaternary organo-onium compounds which can be used in this invention, the nitrogen, phosphorus, arsenic or antimony atom may be a heteroatom in a cyclic structure, e.g., 8-benzyl-1,8-diaza-bicyclo[5,4,0]-7-undecenium chloride. Another class which can be used is amino-phosphonium compounds, some of which are described, for example, in U.S. Pat. No. 4,259,463 (Moggi et al.). Another useful class is phosphorane compounds disclosed, for example, in U.S. Pat. Nos. 3,752,787 (de Brunner) and 4,882,390 (Grootaert et al.). Another class of quaternary organo-onium compounds useful in this invention are iminium compounds, where are also described in said U.S. Pat. No. 4,882,390.

The compounded gum formulation of this invention can also include processing agents, such as those conventionally used to aid in the molding or extrusion of the formulation e.g. carnauba wax or dichlorodiphenyl sulfone, including those of the formula R₁SO₂NHR'', where R₁ is a fluoroaliphatic radical such as a perfluoroalkyl, e.g., C_nF_{2n+1} where n is 4 to 20, or perfluorocycloalkyl, e.g., C_nF_{2n-1} where n is 5 to 20. Another type of processing aid which can be used in this invention is diorgano sulfur oxides, such as those described in U.S. Pat. No. 4,287,320 (Kolb).

Fillers can be mixed with the fluoroelastomer gum to improve molding characteristics and other properties. When a filler is employed, it can be added to the vulcanization recipe in amounts of up to about 100 parts per hundred parts by weight of gum, preferably between about 15 to 50 parts per hundred parts by weight of the gum. Examples of fillers which may be used are reinforcing thermal grade carbon blacks or non-black pigments of relatively low reinforcement characteristics such as clays and barytes.

Fluorocarbon elastomers which can be used in this invention include those described, for example, in the aforementioned prior art, e.g., U.S. Pat. Nos. 3,159,609 (Harris et al.), 3,467,635 (Brasen et al.), 4,214,060 (Apotheker), 4,233,421 (Worm), and 4,263,414 (West). Some of these are commercially available, sold under trademarks such as "Fluorel" and "Viton", and are copolymers whose interpolymers units are generally derived from vinylidene fluoride and one or more other co-monomers. Other useful fluorocarbon elastomers include copolymers of tetrafluoroethylene and propylene, such as those commercially available as AFLASTM elastomers. Among the fluoroelastomer polymers, which may be compounded in accordance with this invention are the elastomeric copolymers whose interpolymers units are derived from two or more of the following fluoromonomers: vinylidene fluoride, hexafluoropropene, chlorotrifluoroethylene, 2-chloropentafluoropropene, fluorinated methyl vinyl ether, tetrafluoroethylene, 1-hydropentafluoropropene, dichlorodifluoroethylene, trifluoroethylene, 1,1-chlorofluoroethylene, and mixtures thereof. Said fluoromonomers may also be copolymerized with other compounds such as non-fluorinated alpha-olefin co-monomers, e.g., ethylene or propylene. The preferred elastomers are copolymers of vinylidene fluoride with at least one terminally ethylenically-unsaturated fluoromonomer containing at least one fluorine atom substituent on each double-bonded carbon atom,

each carbon atom of said fluoromonomer being substituted only with fluorine and optionally with chlorine, hydrogen, lower fluoroalkyl radical, or lower fluoroalkoxy radical; particularly preferred are hexafluoropropene, tetrafluoroethylene, chlorotrifluoroethylene, and 1-hydropentafluoropropene. Particularly preferred are the fluorinated elastomers produced by copolymerizing vinylidene fluoride with hexafluoropropene as described in U.S. Pat. Nos. 3,051,677 (Rexford) and 3,318,854 (Pailthorp et al.), and those copolymers produced by copolymerizing vinylidene fluoride, hexafluoropropene, and tetrafluoroethylene as described in U.S. Pat. No. 2,968,649 (Honn et al.). The elastomeric copolymers of hexafluoropropene and vinylidene fluoride preferably will have between about 15 and about 50 mole percent hexafluoropropene, optionally with the addition of up to 30 mole percent tetrafluoroethylene. Mixtures or blends of elastomers, e.g., of different viscosities, are also suitable.

The relative amounts of the various ingredients in preferred fluorocarbon elastomer compositions of this invention, chosen to provide the desired cure rate and degree of cure, are illustrated for onium curable elastomer compositions and for peroxide curable elastomer systems in the table below. The amount of fluorinated ether composition will vary, but generally will be present in an amount sufficient to impart improved low-temperature properties to the cured composition. Where the fluorinated ether composition is used as a crosslinker, it will generally be present in an amount sufficient to crosslink the gum. The amounts given are in terms of parts per 100 parts by weight of the gum, "phr".

INGREDIENTS	ELASTOMER SYSTEM	
	ONIUM CURABLE	PEROXIDE CURABLE
Fluorinated ether composition of this invention	2-50 phr	2-50 phr
Polyhydroxy compound (crosslinking agent)	0*-5 phr	0
Organo-onium compound (co-curing agent)	0-2 phr	0
Bivalent metal oxide and/or hydroxide (acid acceptor)	2-30 phr	0
Peroxide	0	1-6 phr
TAIC (crosslinking agent)	0	0*-10 phr
Fillers	0-100 phr	0-100 phr

*Note that when the fluorinated ether compositions of the first class (Formula I) are used, it is not required to include crosslinking agents to affect cure.

The aforementioned amounts of the fluorinated ether composition of this invention, which impart improved low-temperature properties to the cured composition, also impart improved mold-release properties to the cured composition. If desired, the amount of the fluorinated ether may be only an amount sufficient to impart improved mold-release properties to the cured composition. Generally, as little as 0.5 phr of the fluorinated ether composition will be sufficient to impart improved mold-release properties.

In accordance with this invention, the desired amounts of compounding ingredients and other conventional adjuvants or ingredients are added to the unvulcanized fluorocarbon gum stock and intimately admixed or compounded therewith by employing any of the usual rubber mixing devices such as Banbury mixers, roll mills, or any other convenient mixing device. The temperature of the mixture on the mill typically will not rise above about 120°C. During milling the components and adjuvants are distributed uniformly throughout the gum. The curing process typically comprises extrusion of the compounded mixture or pressing the compounded mixture in a mold, e.g., a cavity or a transfer mold, and subsequent oven-curing. Pressing of the compounded mixture (press cure) is usually conducted at a temperature between about 95°C and about 230°C, preferably between about 150°C and about 205°C, for a period of from 1 minute to 15 hours, typically from 5 minutes to 30 minutes. A pressure of between about 700 kPa and about 20,600 kPa is usually imposed on the compounded mixture in the mold. The molds first may be coated with a release agent, such as a silicone oil, and prebaked. The molded vulcanizate is then usually post-cured (oven-cured) at a temperature usually between about 150°C and about 315°C., typically at about 232°C, for a period of from about 2 hours to 50 hours or more depending on the cross-sectional thickness of the article. The compositions of this invention can be used to form seals, O-rings, gaskets, etc.

Objects and advantages of this invention are illustrated in the following nonlimiting examples.

TEST METHODS

In the following examples, indicated results were obtained using the following test methods:

- 5 Hardness ASTM D 2240-85 Method A. A Type A-2 Shore Durometer was used. Units reported in parts.
Tensile Strength at Break, Elongation at Break, and Modulus at 100% Elongation. ASTM D 412-75 on sample cut
 from 1.8 mm sheet with ASTM Die D. Units reported in psi.
10% Retraction (TR-10) ASTM D1329. Units reported in °C
Molecular Weight and Functionality Determined by ^{19}F NMR end group analysis.
 10 Mooney Viscosity ASTM 1646-87

In the examples, the preparation of various fluorinated ether compositions and their use as low temperature flexi-
 bilizers (and, in some cases, crosslinking agents) for fluorocarbon elastomer gums are described. In preparing the fluor-
 inated ether compositions, commercially available aliphatic ethers such as those represented by the formula $\text{HO}-$
 15 $(\text{CH}_2\text{CH}_2\text{O})_n-\text{H}$ were converted to the corresponding mono- or di- acetates such as $\text{CH}_3(\text{CO})\text{O}-(\text{CH}_2\text{CH}_2\text{O})_n-(\text{CO})\text{CH}_3$.
 These acetates were then fluorinated by the direct fluorination technique as taught in WO 90/05413 (Costello et al.), or
 by the fluorination technique taught in U.S. Pat. No. 4,894,484 (Lagow et al.). The resulting fluorinated acetates such
 as $\text{CF}_3(\text{CO})\text{O}-(\text{CF}_2\text{CF}_2\text{O})_n-(\text{CO})\text{CF}_3$ were hydrolyzed by treatment with methanol to give methyl esters such as
 $\text{CH}_3\text{O}(\text{CO})\text{CF}_2\text{O}-(\text{CF}_2\text{CF}_2)_n-\text{CF}_2(\text{CO})-\text{OCH}_3$. These methyl esters were then reduced to the corresponding dihydroal-
 20 cools such as $\text{HOCH}_2-\text{CF}_2\text{O}-(\text{CF}_2\text{CF}_2)_n-\text{CF}_2\text{CH}_2\text{OH}$, as described in U.S. Pat. No. 4,094,911 (Mitsch et al.).

Commercially available fluoroelastomer gums were compounded with various ingredients and cured. The physical
 properties of the cured composition were then tested. The gums used were copolymers which, except as otherwise
 indicated, have the weight percents of interpolymers derived from the monomers shown below. Gum D also
contains a minor amount of a bromine-containing cure-site monomer.

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WEIGHT % MONOMERS					
GUM	$\text{CF}_2=\text{CH}_2$	$\text{CF}_2=\text{CFCF}_3$	$\text{CF}_2=\text{CF}_2$	$\text{CH}_2=\text{CHCH}_3$	$\text{CF}_2=\text{CFOCF}_3$
A	62	38	--	--	--
B	42	34	24	--	--
C	32	--	40	28	--
35 D	62	38	--	--	--
E	59	--	6	--	35
F	32	--	40	28	--
40 G	41	--	20	--	39
H	--	--	73	27	--

PREPARATION 1 (not within scope of appended claims)

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A fluorinated ether composition comprising the structure $\text{HO}-\text{CH}_2-\text{CF}_2-\text{O}-(\text{CF}_2\text{CF}_2\text{O})_n-\text{CF}_2-\text{CH}_2-\text{OH}$, having an
average molecular weight of 1500, and an average hydroxyl functionality of 1.8, was prepared by direct fluorination of
 polyethylene glycol diacetate (Aldrich Chemical, Milwaukee, WI).

To 100 parts of fluoroelastomer gum A, was added 0.5 phr of triphenylbenzyl phosphonium chloride, followed by 30
 50 phr of carbon black, 3 phr of MgO and 6 phr of $\text{Ca}(\text{OH})_2$ using a two-roll mill. To this compounded mixture was added
 20 phr of the fluorinated ether composition described above. Milling continued until a homogeneous blend formed. The
 gum was press-cured for 15 minutes at 177°C and then post-cured for 24 hours at 204°C .

COMPARATIVE EXAMPLE 1-C

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For comparative purposes, the fluoroelastomer gum A was compounded, milled, press-cured, and post-cured as in
 Prep'n 1, substituting 2 phr of Bisphenol AF for the fluorinated ether composition.

PREPARATION 2 (not within scope of appended claims)

A fluorinated ether composition comprising structure $\text{HO-CH}_2\text{-(CF}_2\text{)}_3\text{-O-(CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{O)}_n\text{-(CF}_2\text{)}_3\text{-CH}_2\text{-OH}$, having an average molecular weight of 850, and an average hydroxyl functionality of 1.64, was prepared from poly(tetramethyleneoxide) diol (commercially available from BASF) by direct fluorination.

EXAMPLE 1

In this example, a fluorinated ether composition comprising the structure $\text{H}_2\text{N-CH}_2\text{-CF}_2\text{-O-(CF}_2\text{CF}_2\text{O)}_n\text{-CF}_2\text{-CH}_2\text{-NH}_2$, having an average molecular weight of 615, and an average amino functionality of 1.21, was prepared by reduction of the amide composition comprising the structure $\text{H}_2\text{N-CO-CF}_2\text{-O-(CF}_2\text{CF}_2\text{O)}_n\text{-CF}_2\text{-CO-NH}_2$. The amide composition was prepared from the reaction of ammonia with the corresponding fluorinated methyl ester composition.

100 parts by weight of fluoroelastomer gum A was compounded, milled, press-cured, and post-cured as in Prep'n 1, using 20 phr of the above fluorinated ether composition. The results of the tests are shown in Table 1.

COMPARATIVE EXAMPLE 2-C

For comparative purposes, the fluoroelastomer gum A was compounded as before, substituting 1.0 phr of diamino-carbamate (DIAC) for the fluorinated ether composition of Example 1 and omitting the triphenylbenzyl phosphonium chloride. The gum was cured as previously described, and tested. The results are shown in Table 1.

EXAMPLE 2

A fluorinated ether composition comprising the same structure as in Example 1, having an average molecular weight of 763, and an average amino functionality of 1.74, was prepared as in Example 1.

100 parts by weight of fluoroelastomer gum A was compounded, milled, press-cured, and post-cured as in Prep'n 1, using 20 phr of the above fluorinated ether composition. The results of the tests are shown in Table 1.

TABLE 1

Example	Fluorinated Ether Composition (Crosslinker) Amount (phr)	Hardness	100% Modulus	Tensile	% Elongation	TR-10 (°C)
1	20	74	490	2330	300	-22.2
2	20	77	1140	2280	160	-25.0
Comparative	DIAC (Crosslinker)					
2-C	1	75	900	2000	200	-17.8

Table 1 shows that fluorinated ether compositions with amino functionality can be used, in conjunction with an accelerator such as triphenylbenzyl phosphonium chloride, as crosslinking agents in fluoroelastomer gums to improve the low-temperature performance while retaining the physical properties of the cured gum. Examples 1 and 2 have lower TR-10 than Comparative Example 2-C, but still have a desirable range of hardness, modulus, tensile, and elongation properties.

EXAMPLE 3

A fluorinated ether composition comprising the structure $\text{CH}_2=\text{CHCH}_2\text{O-CH}_2\text{CF}_2\text{-O-(CF}_2\text{CF}_2\text{O)}_n\text{-CF}_2\text{CH}_2\text{-OCH}_2\text{CH=CH}_2$, having an average molecular weight of 776, and an average allyl functionality of 1.56, was prepared by treatment of the fluorinated ether composition of Prep'n 1 with allyl bromide.

To 100 parts by weight of gum F, a peroxide curable fluoroelastomer gum, was added 30 phr of carbon black, 3 phr of Ca(OH)_2 , and 2.5 phr of Luperco 101XL (available from Lucidol Corp.) using a two roll mill. To this compound mixture was added 20 phr of the above fluorinated ether composition. Milling continued until a homogeneous blend formed. The gum was press-cured for 15 minutes at 177°C and then post-cured for 24 hours at 204°C. The results of the tests are shown in Table 2.

EXAMPLE 4

100 parts by weight of fluoroelastomer gum VITON™ VTR-6279 (available from DuPont) was blended with 30 phr of carbon black, 3 parts of $\text{Ca}(\text{OH})_2$ and 2.5 parts of Luperco 101XL. To this compounded mixture was added 20 phr of the fluorinated ether composition of Example 3, using a two-roll mill. Milling continued until a homogeneous blend formed. The compounded gum was press-cured for 15 minutes at 177°C and post-cured for 24 hours at 204°C. The results of the tests are shown in Table 2.

COMPARATIVE EXAMPLE 3-C

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For comparative purposes the gum VITON™ VTR-6279 was compounded as in Example 4 omitting the fluorinated ether composition and using 2.5 phr of triallylisocyanurate (TAIC) as the crosslinking agent. The gum was then cured and tested as in Example 3. The results of the tests are shown in Table 2.

15 COMPARATIVE EXAMPLE 4-C

For comparative purposes, gum F was compounded as in example 3, substituting 3 phr of triallylisocyanurate (TAIC) as the crosslinking agent. The gum was cured and tested as in Example 3. The results of the tests are shown in Table 2.

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EXAMPLE 5

100 parts by weight of fluoroelastomer gum D was compounded, milled, press-cured, and post-cured as in example 3 using 20 phr of the fluorinated ether composition of Example 3. The results of the tests are shown in Table 2.

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COMPARATIVE EXAMPLE 5-C

For comparative purposes, the fluoroelastomer gum D was compounded as in Example 3, substituting 3 phr of triallylisocyanurate (TAIC) as the crosslinking agent. The gum was cured and tested as in Example 3. The results of the tests are shown in Table 2.

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EXAMPLE 6

100 parts by weight of fluoroelastomer gum D was compounded, milled, press-cured, and post-cured as in Example 3, using 5 phr of the fluorinated ether composition of Example 3. The results of the tests are shown in Table 2.

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EXAMPLE 7

The fluorinated ether composition comprising the structure $\text{CH}_2=\text{CHCH}_2\text{-NHC(O)-CF}_2\text{O-(CF}_2\text{CF}_2\text{O)}_n\text{-CF}_2\text{-C(O)NH-CH}_2\text{CH=CH}_2$, having an average molecular weight of 895, and an average allyl functionality of 1.56, was prepared by the reaction of the corresponding fluorinated methyl ester composition with allylamine.

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100 parts by weight of fluoroelastomer gum D was compounded, milled, press-cured, and post-cured as in Example 3, using 20 phr of the above fluorinated ether composition. The results of the tests are shown in Table 2.

45 EXAMPLE 8

A fluorinated ether composition comprising structure $\text{CH}_2=\text{CHCH}_2\text{OCH}_2\text{-(CF}_2\text{)}_3\text{O-(CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{O)}_n\text{-(CF}_2\text{)}_3\text{CH}_2\text{-OCH}_2\text{CH=CH}_2$, having an average molecular weight 610, and an average allyl functionality of 1.96, was prepared by treatment of the fluorinated ether composition of Prep'n 2 with allyl bromide.

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100 parts by weight of fluoroelastomer gum D compounded, milled, press-cured, and post-cured as in Example 3, using 10 phr of the above fluorinated ether composition. The results of the tests are shown in Table 2.

EXAMPLE 9

100 parts by weight of fluoroelastomer gum D was compounded, milled, press-cured, and post-cured as in Example 3, using 5 phr of the fluorinated ether composition of Example 8. The results of the tests are shown in Table 2.

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EXAMPLE 10

100 parts by weight of fluoroelastomer gum G, a peroxide curable fluoroelastomer gum, was compounded, milled, press-cured, and post-cured as in Example 3, using 20 phr of the fluorinated ether composition of Example 3. The results of the tests are shown in Table 2.

COMPARATIVE EXAMPLE 6-C

For comparative purposes, fluoroelastomer gum G was compounded as in Example 3, substituting 3 phr of TAIC as the crosslinking agent. The gum was cured and tested as in Example 3. The results are shown in Table 2.

EXAMPLE 11

100 parts by weight of fluoroelastomer gum E, a peroxide curable fluoroelastomer gum, was compounded, milled, press-cured, and post-cured as in Example 3, using 20 phr of the fluorinated ether composition of Example 3. The results of the tests are shown in Table 2.

COMPARATIVE EXAMPLE 7-C

For comparative purposes, the fluoroelastomer gum E was compounded, milled, press-cured, and post-cured as in Example 3, substituting 3.0 phr TAIC as the crosslinking agent. The gum was cured and tested as before and the results shown in Table 2.

TABLE 2

Example	Fluoro Elastomer Gum	Fluorinated Ether Composition (Crosslinker) Amount (phr)	Hardness	100% Modulus	Tensile	% Elongation	TR-10 (°C)
3	F	20	65	160	1800	320	-16.1
4	VITON™	20	71	395	1660	200	-19.4
5	D	20	65	240	1640	400	-23.3
6	D	5	65	275	1940	360	-23.3
7	D	20	65	280	1395	340	-22.2
8	D	10	65	230	2095	360	-22.8
9	D	5	72	385	2740	260	-20.6
10	G	20	67	320	1960	160	-30.0
11	E	20	64	895	2235	380	-32.8
Comparative		TAIC (Crosslinker)					
3-C	VITON™	2.5	79	1030	3160	220	-10.0
4-C	F	3	71	430	2115	250	-11.7
5-C	D	3	75	900	2000	200	-19.4
6-C	G	3	74	1024	2249	168	-24.8
7-C	E	3	64	320	1465	350	-31.1

Table 2 shows that fluorinated ether compositions with allyl functionality can be used as crosslinking agents in fluoroelastomer gums to improve low-temperature performance of the cured gum, while retaining the other desired physical properties.

PREPARATION 3 (not within scope of appended claims)

A fluorinated ether composition comprising the structure $\text{CF}_3\text{-O-(CF}_2\text{CF}_2\text{O)}_n\text{-CF}_2\text{CH}_2\text{-OH}$, having an average molecular weight of 920, and an average hydroxyl functionality of 0.92, was prepared by direct fluorination, as in Prep'n 1, of poly(ethylene glycol) monomethyl ether (available from Aldrich).

To 100 parts by weight of fluoroelastomer gum A was added 0.5 phr of triphenylbenzyl phosphonium chloride, followed by 30 phr of carbon black, 3 phr of MgO, 6 phr of Ca(OH)_2 , and 2 phr of Bisphenol-AF using a two roll mill. To this compounded mixture was added 10 phr of the above fluorinated ether composition. Milling continued until a homogeneous blend formed. The gum was press-cured for 15 minutes at 177°C and then post-cured for 24 hours at 204°C.

PREPARATION 3A (not within scope of appended claims)

A fluorinated ether composition comprising the same structure as in Prep'n 3, having an average molecular weight of 700, and an average hydroxyl functionality of 0.98, was prepared as in Example 28.

100 parts by weight of fluoroelastomer gum A was compounded, milled, press-cured and post-cured as in Prep'n 3 using 15 phr of the above fluorinated ether composition.

EXAMPLE 12

A fluorinated ether composition comprising the structure $\text{CF}_3\text{-O-(CF}_2\text{CF}_2\text{O)}_n\text{-CF}_2\text{CH}_2\text{-O-CH}_2\text{CH=CH}_2$, was prepared from the fluorinated ether composition of Prep'n 3 by treatment with allyl bromide. The resulting composition had an average molecular weight of 948 and an average allyl functionality of 0.92.

To 100 parts by weight of fluoroelastomer gum VITON™ VTR-6279 (available from DuPont) was added 30 phr of carbon black, 2 phr of Ca(OH)_2 , 2.5 phr of Luperc 101XL, and 2.5 phr TAIC using a two-roll mill. To this compounded mixture was added 20 phr of the above fluorinated ether composition. Milling was continued until a homogeneous blend was formed. The compounded gum was press-cured and post cured as in Example 4. The results of the tests are shown in Table 3.

TABLE 3

Example	Fluoro Elastomer Gum	Fluorinated Ether Composition Amount (phr)	Hardness	100% Modulus	Tensile	% Elongation	TR-10 (°C)
Prep'n 3	A	15.0	78	956	2240	150	-23.9
Prep'n 3A	A	15.0	77	860	2235	160	-21.1
12	VITON™	20.0	74	685	2825	220	-16.7
Comparative							
1-C	A	---	79	900	2000	200	-17.8
3-C	VITON™	---	79	1030	3160	220	-10.0

Table 3 shows that monofunctional fluorinated ether compositions can be used in conjunction with a conventional crosslinking agent, such as Bisphenol AF or TAIC, to improve the low-temperature performance of cured fluoroelastomer gums while retaining the other desired physical properties.

Compounded gums in the following Examples 13 to 16 and Comparative Examples 8-C to 11-C were prepared and their release properties evaluated. A 2.5 cm x 2.5 cm x 1.3 mm thick coupon of each compounded gum was press-cured in a clean mold, cooled, and then peeled out of the mold by hand. The ease or difficulty in peeling the samples out of the mold was evaluated comparatively, assigning a mold-release value of from zero to 4, with a 4 representing the easiest release characteristics.

The press-cured samples were weighed, post-cured, and re-weighed to give the percent weight loss of the sample. Three gums were used (A, D, and H). For each gum an initial composition was made and then further compositions of the same composition were made except with additional materials. The initial compositions are Comparative Examples 8-C, 10-C, and 11-C. By comparing the percent weight losses of the initial compositions with compositions containing additional materials, and by assuming that any increase in percent weight loss was due to loss of the additional mate-

rials, the percent weight loss of the additional materials was calculated.

Compression set of cured compounded gums was determined after 70 hours at 200°C using ASTM D395 method B using a 2.5 cm inside diameter O-ring with a 3.5 mm cross section.

The results of all these evaluations are shown in Table 4.

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Comparative Example 8-C

To 100 parts of fluoroelastomer gum A, using a two-roll mill, was added 0.5 phr of triphenylbenzyl phosphonium chloride, followed by 30 phr of carbon black, 3 phr of MgO, and 6 phr of Ca(OH)₂. To this compounded mixture, 2.0 phr of Bisphenol-AF were milled. Milling continued until a homogeneous blend formed. The gum was press-cured for 15 minutes at 177°C and then post-cured for 24 hours at 232°C.

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Comparative Example 9-C

Fluoroelastomer gum A was compounded as in Comparative Example 8-C, with the addition of 2.5 phr of dichlorodiphenyl sulfone as mold release agent. This compounded mixture was press-cured and post-cured as in Comparative Example 8-C.

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PREPARATION 4 (not within the scope of the appended claims)

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A fluorinated ether composition comprising the structure $\text{CF}_3\text{-O-(CF}_2\text{CF}_2\text{O)}_n\text{CF}_2\text{CH}_2\text{-OH}$, having an average molecular weight of 398 and an average hydroxyl value of 1, was prepared by direct fluorination of poly(ethylene glycol) monomethyl ether (available from Aldrich).

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Fluoroelastomer gum A was compounded as in Comparative Example 8-C, with the addition of 4.0 phr of the above fluorinated ether composition. Milling continued until a homogeneous blend formed. The gum was press-cured and post-cured as in Comparative Example 8-C.

PREPARATION 5 (not within the scope of the appended claims)

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A fluorinated ether composition comprising the structure $\text{HO-CH}_2\text{-CF}_2\text{-O-(CF}_2\text{CF}_2\text{O)}_n\text{CF}_2\text{CH}_2\text{-OH}$, having an average molecular weight of 956 and an average hydroxyl value of 1.56, was prepared by direct fluorination of poly(ethylene glycol) (available from Aldrich).

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Fluoroelastomer gum A was compounded as in Comparative Example 8-C, with the addition of 4.0 phr of the above fluorinated ether composition. Milling continued until a homogeneous blend formed. The gum was press-cured and post-cured as in Comparative Example 8-C.

Comparative Example 10-C

To 100 parts of fluoroelastomer gum D (a peroxide curable fluoroelastomer gum) was added 2.5 phr of Lupercol 101XL peroxide (available from Lucidol Corp.), followed by 30 phr of carbon black, 3 phr of Ca(OH)₂, and 2.5 phr of triallylisocyanurate. Milling continued until a homogeneous blend formed. The gum was press-cured and post-cured as in Comparative Example 8-C.

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Example 13

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A fluorinated ether composition comprising the structure $\text{CF}_3\text{-O-(CF}_2\text{CF}_2\text{O)}_n\text{CF}_2\text{CH}_2\text{-OCH}_2\text{CH=CH}_2$, having an average molecular weight of 948 and an average allyl functionality of 1.0, was prepared by treatment of the fluorinated ether composition of Prep'n 4 with allyl bromide.

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Fluoroelastomer gum D was compounded as in comparative Example 10-C, with the addition of 3 phr of the above fluorinated ether composition. Milling continued until a homogeneous blend formed. The gum was press-cured and post-cured as in Comparative Example 8-C.

Example 14

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A fluorinated ether composition comprising the structure $\text{CH}_2\text{=CHCH}_2\text{-O-CH}_2\text{CF}_2\text{-O-(CF}_2\text{CF}_2\text{O)}_n\text{CF}_2\text{CH}_2\text{-OCH}_2\text{CH=CH}_2$, having an average molecular weight of 776 and an average allyl functionality of 1.6, was prepared by treatment of the fluorinated ether composition of Prep'n 5 with allyl bromide.

Fluoroelastomer gum D was compounded as in Comparative Example 10-C with the addition of 3 phr of the above

fluorinated ether composition. Milling continued until a homogeneous blend formed. The gum was press-cured and post-cured as in Comparative Example 8-C.

Example 15

A fluorinated ether composition having the same structure as in Example 14 except having an average molecular weight of 1220 and an average allyl functionality of 1.67, was prepared as in Example 14. Fluoroelastomer gum D was compounded as in Comparative Example 10-C with the addition of 4.0 phr of the above fluorinated ether composition, then press-cured and post-cured as in Comparative Example 8-C.

Comparative Example 11-C

To 100 parts of fluoroelastomer gum H (a peroxide curable fluoroelastomer gum) was added 30 phr of carbon black, 3 phr of $\text{Ca}(\text{OH})_2$, 4 phr of 40% active α, α -bis-[t-butylperoxy]diisopropyl benzene (commercially available as Vulkup™ 40KE), 4 phr triallylisocyanurate, 1 phr of carnauba wax and 1 phr of Span 60™ sorbitan monostearate. Milling continued until a homogeneous blend formed. The gum was press-cured and post-cured as in Comparative Example 8-C.

Example 16

Fluoroelastomer gum H was compounded as in Comparative Example 11-C. with the addition of 3 phr of the diallyl ether of Example 15. Milling continued until a homogeneous blend formed. The gum was press-cured and post-cured as in Comparative Example 8-C.

TABLE 4

Example	Mold Release Value	% Weight Loss of Additional	Compression Set, %
13	2	23	46
14	1	17	50
15	2	5	47
16	4	0	56
8-C	0	---	17
9-C	3	100	17
10-C	0	---	37
11-C	0	---	66

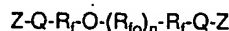
The data in Table 4 show that the compositions of this invention can provide cured gums with excellent mold release and which do not volatilize or increase the compression set significantly. The molding of conventional fluoroelastomer compounds generally requires the addition of processing agents or mold release additives at the molding step. A general deficiency of current commercial additives is that they either volatilize or cause an increase in compression set. Volatilization is undesirable because it may create pollution problems and shrinkage of the molded part. In Comparative Example 9-C dichlorodiphenyl sulfone was added and, although the mold release was excellent, the dichlorodiphenyl sulfone was volatilized.

Many conventional fluoroelastomers generally exhibit a tendency to become "scorchy", i.e., they cure prematurely or too rapidly when compounded. The curing is effected at an elevated temperature by milling in the curing agent and allowing sufficient time at the elevated temperature for the curing agent to react with the elastomer. Although use of many curing agents satisfy the physical properties requirement of the ultimate product by increasing its tensile strength, hardness and elongation, often some undesirable side effects are observed during curing. One of these side effects is called "scorch". Scorch is a function of the activity of the curing agent and the temperature utilized and is said to be the result of too fast or premature curing at some point prior to the final curing of the end product. In the present invention it has been found that the selection of the acid acceptor can decrease the tendency of the compounded gum to scorch. The suitability of a particular acid acceptor depends on the particular crosslinking agent used and can be evaluated by using ASTM D-1566 (which measures Mooney scorch).

Claims

1. A fluorocarbon elastomer composition comprising a fluorocarbon elastomer gum, and fluorinated ether composition comprising a functional fluoroaliphatic mono- or polyether of linear and regular structure, wherein said functionality is reactive with said gum and is selected from the group consisting of primary amino, and allyl ($-\text{CH}_2-\text{CH}=\text{CH}_2$).

2. The composition of claim 1 wherein said fluorinated ether composition comprises the structure



with an (average molecular weight) between 250 and 3,000;

where Z is a group reactive with said fluorocarbon elastomer gum, the average number of said Z groups per fluorinated ether molecule in said ether composition being greater than 1.0 and less than or equal to 2.0, said Z group being selected from the group consisting of primary amino, and allyl ($-\text{CH}_2-\text{CH}=\text{CH}_2$);

Q is a divalent linking group;

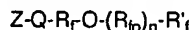
R_f is a non-branched, perfluoroalkyl group of 1 to 20 carbon atoms;

R₁₀ is a perfluoroalkyleneoxy group selected from the group consisting of $-(\text{CF}_2)_2\text{-O-}$, $-(\text{CF}_2)_3\text{-O-}$, $-(\text{CF}_2)_4\text{-O-}$, $-\text{CF}_2\text{-CF}_2\text{-O-CF}_2\text{-O-}$, $-\text{CF}_2\text{-CF}_2\text{-O-CF}_2\text{-CF}_2\text{-O-CF}_2\text{-O-}$;

n is a number from 0 to 30.

3. The composition of claim 2 wherein Q is selected from the group consisting of $-\text{CO-}$, $-\text{SO}_2\text{-}$, $-\text{O-}$, $-\text{C}_y\text{H}_{2y}\text{-}$ where y is 1 to 20, $-\text{C}_6\text{H}_4\text{-}$, $-\text{C}_6\text{H}_3\text{Cl-}$, $-\text{OC}_2\text{H}_4\text{-}$, $-\text{CONR-}$ or $-\text{SO}_2\text{NR-}$ where R is lower alkyl of 1 to 3 carbon atoms, or combinations thereof, and wherein when Q is said $-\text{CO-}$, $-\text{O-}$, $-\text{SO}_2\text{-}$, $-\text{CONR-}$, or $-\text{SO}_2\text{NR-}$, Z is allyl.

4. The composition of claim 1 wherein said fluorinated ether composition comprises the structure



with an average molecular weight between 250 and 3,000;

where Z is a group reactive with said fluorocarbon elastomer gum, the average number of said Z groups per fluorinated ether molecule in said ether composition being less than or equal to 1.0, said Z group being selected from the group consisting of primary amino, and allyl ($-\text{CH}_2-\text{CH}=\text{CH}_2$); Q is a divalent linking group;

R'₁ is a nonbranched, monovalent, perfluoroaliphatic fluorocarbon containing from 1 to 10 carbon atoms;

R_f is a non-branched, perfluoroalkyl group of 1 to 20 carbon atoms,

R₁₀ is a perfluoroalkyleneoxy group selected from the group consisting of $-(\text{CF}_2)_2\text{-O-}$, $-(\text{CF}_2)_3\text{-O-}$, $-(\text{CF}_2)_4\text{-O-}$, $-\text{CF}_2\text{-CF}_2\text{-O-CF}_2\text{-O-}$, $-\text{CF}_2\text{-CF}_2\text{-O-CF}_2\text{-CF}_2\text{-O-CF}_2\text{-O-}$;

n is a number from 0 to 30.

5. The composition of claim 2 where R₁₀ is $-\text{CF}_2\text{-CF}_2\text{-O-}$.

6. The composition of claim 4 where R₁₀ is $-\text{CF}_2\text{CF}_2\text{-O-}$.

7. The composition of claim 1 or claim 4 further comprising a curing system.

8. The composition of claim 7 wherein said curing system comprises a peroxide.

9. The composition of claim 7 wherein said curing system comprises ZnO.

10. The composition of claim 9 further comprising PbO or dibasic lead phosphite.

11. The composition of claim 1 wherein the amount of said fluorinated ether composition present is 0.5 to 50 weight percent based on the weight of said gum.

12. A composition according to claim 1 or claim 4 further comprising a cross-linking agent.

13. The composition of claim 2 wherein said fluorinated ether composition is present in an amount sufficient to cross-

link said gum.

14. The composition of claim 1 wherein said gum comprises a polymer whose interpolymerized units comprise units derived from two or more of the following monomers, $\text{CF}_2=\text{CH}_2$, $\text{CF}_2=\text{CFCF}_3$, $\text{CF}_2=\text{CF}_2$, $\text{CH}_2=\text{CHCH}_3$, $\text{CF}_2=\text{CFOCF}_3$.
15. The composition of claim 1 wherein said gum comprises a copolymer of vinylidene fluoride, hexafluoropropene, and, optionally, tetrafluoroethylene.
16. The composition of claim 1 wherein said gum comprises a copolymer of vinylidene fluoride, tetrafluoroethylene, and propylene.
17. A method of preparing an elastomer composition, said method comprising mixing a fluorocarbon elastomer gum, and a fluorinated ether composition comprising a functional fluoroaliphatic mono- or polyether of linear and regular structure, wherein said functionality is reactive with said gum and is selected from the group consisting of primary amino, and allyl ($-\text{CH}_2-\text{CH}=\text{CH}_2$).
18. A method according to claim 17 wherein said fluorinated ether composition is as defined in claim 1 or claim 4.
19. A method of forming a cured elastomeric article, comprising the steps of:
 - 1) shaping, at an elevated temperature into the form of an article, a compounded curable fluorocarbon elastomer composition, said elastomer composition being defined as in claim 1, and
 - 2) heating said formed article to cure said compounded composition.
20. A method according to claim 19 wherein the compounded curable elastomer composition further comprises a cure system for said gum.
21. A shaped article comprising the composition of claim 1 in its cured state.